PREFACE

Heterogeneous catalytic reactions involve multiple steps that may include adsorption, surface reactions and desorption of products and reactants The identification of these steps as well as the chemical species involved is the key to understand the functioning of a heterogeneous catalyst Zeolites are microporous materials with pore dimensions of the order of few molecular diameters They find extensive applications as heterogeneous catalysts and adsorbents in many industrial processes The knowledge of conformation, location and reactivity of guest species within the zeolite is vital to understand the kinetics and mechanism of zeolite catalyzed reactions and hence their optimal functioning as catalysts In this thesis, the adsorption and reactivity of small organic molecules in microporous zeolites have been studied The nature and concentration of the adsorbed species, reactants as well as products, within the zeolite have been monitored *in-situ* as a function of a programmed temperature rise by Fourier-Transform Infrared (FTIR) reflectance spectroscopy while the desorbing or evolving species have been simultaneously analyzed by a quadrupole mass spectrometer The latter experiment corresponds to a Temperature Programmed Desorption (TPD) measurement **Chapter 1** and **2** provides an introduction to the materials and methods used in the present study

The sorption of benzene over the MFI zeolite, H-ZSM-5, with varying Si/Al ratios, is described in **Chapter 3** The objective was to delineate and evaluate the relative importance of the Bronsted sites as compared to non-Bronsted sites in the straight, sinusoidal (zig-zag) channels and intersection voids of the zeolite The combined FTIR and TPD studies showed that the Bronsted sites are the preferred adsorption sites at low adsorbate concentration and it is only at higher loading that benzene occupies the intersection voids These results were inferred from the fact the TPD of benzene over H-ZSM-5 showed two maxima, with the lower temperature desorption maxima appearing only at higher loading The relative magnitude of the high temperature maxima decreased with increasing Si/Al ratio and was completely absent in silicalite-1, the purely siliceous form of ZSM-5 The infra-red spectra of adsorbed species associated with the higher temperature TPD maxima is characteristic of benzene adsorbed on a Bronsted site

The dimension and topology of the zeolitic voids can influence the conformational geometry of a guest molecule when the dimensions of the two are comparable In **Chapter 4** the adsorption of cyclohexane that has a kinetic diameter (6 Å) comparable to that of the intersection voids of ZSM-5 (8 7 Å) has been investigated Infra-red and Raman spectroscopy has been used to establish the conformation of the flexible cyclohexane molecule adsorbed in ZSM-5 The results have been compared with those for cyclohexane adsorbed in the much larger voids of zeolite-Y where it is known to exist exclusively in the chair conformer In ZSM-5 two conformers of cyclohexane in thermal equilibrium are observed, one of which lacks a center of inversion and is the thermodynamically more stable form Molecular modeling studies support the experimental observations In ZSM-5, a distorted-chair conformer is found to be more stable as compared to the chair conformer, while in zeolite-Y the opposite is true

The kinetic diameters of benzene (5 9 Å) and cyclohexane (6 Å) are similar to the size of the channel system of ZSM-5 (intersections -8 7 Å and channel openings - 5 5-5 7 Å), but while benzene is rigid, cyclohexane is flexible The co-adsorption of benzene and cyclohexane in H-ZSM-5 has been investigated **Chapter 5** The objective of the study was to investigate whether flexibility would confer any additional advantage for adsorption on the non-Bronsted sites of the zeolite The results, however, showed that no such advantage operated In the intersection voids of H-ZSM-5 the relative concentration of benzene and cyclohexane was statistical and dependent only on the initial gas phase concentrations There is, however, evidence that when benzene is present the adsorption of cyclohexane occurs at a site different from that occupied when cyclohexane is adsorbed as a single component

Chapter 6 deals with a detailed study of the adsorption and conformation of *n*-alkanes, C_5-C_8, in zeolites of differing pore size, void dimension and connectivity using FTIR and TPD measurements The focus of the study was on conformational changes as a function of loading, temperature and the structure of the zeolite The alkane methylene stretching modes in the infrared spectra, that are sensitive to chain conformation, have been used to monitor changes in conformation of the confined alkane A characteristic feature of the *n*-alkane TPD profile in all the zeolites investigated was the appearance of a second desorption maxima at increased alkane loading The temperature of the second desorption peak was found to depend on the chain length of the alkane and the structure of the zeolite Structural

considerations rule out the possibility of differing adsorption sites as the reason for the two peaks in the TPD Although there are conformational changes with loading, no significant change in conformation is associated with the second desorption maxima It is shown that the appearance of the second peak in the TPD is due to a loss of translational mobility of the adsorbed alkane molecules that manifests above a critical adsorbate loading

The ring *versus* side-chain alkylation of toluene by methanol over alkali-exchanged zeolite-X of differing basicity has been investigated in **Chapter 7** Over the basic Cs-exchanged zeolite the product of alkylation is styrene /ethylbenzene while over the acidic Li-exchanged zeolite, ring alkylation occurs to give mainly xylene as the product FTIR and TPD investigations reveal that, the key difference in the two types of alkylation processes is in the state of the adsorbed methanol present at temperatures above 550 K In basic zeolites, methanol decomposes to formaldehyde and formates The former is the key 'side-chain' alkylating species that leads to the formation of styrene In the acidic zeolites it is shown that methanol bound to the acid sites plays an active role in the 'ring alkylation' of toluene to xylene